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(54) Title: PROCESS FOR THE TREATMENT OF WASTE METAL CHLORIDES

(57) Abstract: A process is described for treating the residues from metal chlorination processes wherein valuable volatile metal chlorides or metalorgano chlorides are recovered while low volatility metal chlorides and chloride complexes are reacted with a neutralizing humectant. The resulting neutral, dry solid is suitable for land fill disposal or for recovery of valuable metal constituents by extractive metallurgy techniques.

WO 2004/096707 A1

- 1 -

**PROCESS FOR THE TREATMENT OF WASTE METAL CHLORIDES**

This claims the benefit of U.S. Provisional Application No. 60/459,867, filed April 1, 2003, which application is incorporated herein by reference.

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**Background and Summary**

The present invention relates to processes for rendering a solid residue material non-reactive to the normal ambient environment. It is particularly applicable to systems wherein a desired moisture-reactive volatile compound has been separated from a less  
10 volatile residue which then is discharged for disposal. Recovery of valuable and useful materials from the residue may be possible.

In the production of chlorosilanes, organochlorosilanes, titanium chlorides and other metal chlorides such as hafnium and zirconium chlorides, an impure solid metal or metal oxide of the primary product chloride is consumed. The impurities in the raw  
15 metal or metal oxide may or may not be reacted, but are rejected from the process as a solid mixture or slurry containing unreacted starting material, concentrated impurities from the starting material, chlorides of the impurity metal constituents and unrecovered chloride product. These combined residue mixtures when exposed to ambient atmosphere produce corrosive hydrogen chloride gas or hydrochloric acid and may also  
20 be flammable.

Examples of such procedures are the production of trichlorosilane, dichlorosilane and silicon tetrachloride by the hydrochlorination of silicon, the production of trichlorosilane by the hydrogenation of silicon tetrachloride over silicon metal, the production of silicon tetrachloride by chlorination of quartz, the production of  
25 organochlorosilanes by reaction of organochlorides, such as methyl and benzyl chloride with silicon, the production of titanium tetrachloride by chlorination of rutile ore, and the production of zirconium and hafnium chlorides by the chlorination of zircon containing sand.

In these processes, the unreacted portion of the raw material metal or metal  
30 oxide, which is sometimes referred to as "ash," is rejected. The rejected material consists of a slurry mixture of insoluble metal, metal oxide, low volatility, water-reactive metal chlorides and a liquid phase of potentially recoverable product.

- 2 -

By metal chlorides are meant chemical compounds such as aluminum chloride, titanium chloride, vanadium chloride, chromium chloride, manganese chloride, iron chloride, cobalt chloride, nickel chloride, copper chloride and zinc chloride. Those skilled in the art will recognize additional members of this group of low volatility, water-  
5 reactive metal chlorides. Such additional metal chlorides have a boiling point greater than 150°C at atmospheric pressure and react upon contact with water to produce HCl.

The slurry is corrosive when exposed to moist air, flammable when dry and may contain environmentally hazardous components. Disposal of these metal/metal oxide/metal chloride mixtures requires that they be rendered non-reactive with air or  
10 moisture and be stabilized against mild acid leaching of the hazardous metal components. The residues may also contain valuable catalytic metals whose loss would be a significant economic penalty on the process.

In this disclosure, the discussion focuses on the production of trichlorosilane by hydrogenation of silicon tetrachloride. However, it should be appreciated by those skilled in the art that the described principals and practices would apply to all of the  
15 aforementioned processes which generate chloride containing metal and metal chloride residues and to other procedures where a moisture-reactive volatile compound and a solid residue are to be separated with the volatile compound to be recovered and the solid residue material is needed to be rendered non-reactive to the normal ambient  
20 environment.

Chlorosilanes such as trichlorosilane and silicon tetrachloride are prepared by reacting crude silicon with chlorine or hydrogen chloride. Trichlorosilane can also be prepared by the reaction of silicon tetrachloride and hydrogen with crude silicon. In common industrial processing, for example as described in U.S. Patent 3,878,291  
25 (Keller) and U.S. Patent 4,676,967 (Breneman), the crude silicon is of the type which has a silicon content greater than about 85% by weight.

The impurities in the crude silicon are mainly iron, aluminum, calcium, manganese, and titanium which are converted to their respective chlorides in an analogous method as the production of the chlorosilanes. In addition to these metals,  
30 other purposefully added metals may be present as catalysts and promoters. Such added active metals are copper, zinc, silver, and nickel. All of the non-silicon materials are rejected from the process as a "residue" or ash. Also, during the distillation purification

- 3 -

of the chlorosilanes a residue fraction is generated. This distillation residue can contain fine particles of silica, higher boiling polychlorosilanes and traces of high boiling organic materials that may have been used as catalysts or promoters in other parts of the chlorosilane production process.

5 Customarily, the residues that result from the direct reaction and distillation purification are presented in the form of a slurry or suspension of solids and higher boiling liquids containing sufficient chlorosilanes to maintain fluidity. This stream requires additional processing to render it non-reactive or non-hazardous before it can be ready for environmentally safe disposal.

10 The distillation of the chlorosilanes is carried out as completely as possible because any chlorosilanes remaining in the residue can no longer be converted into useful products and therefore represent a loss in value. In those instances where the residues to be disposed of are in the form of a suspension, the solid fraction consists of unreacted silicon metal, silica and other metals and non-silicon metal chlorides. The  
15 solids are slurried in a liquid phase which contains 50 – 80% silicon tetrachloride and/or trichlorosilane and 1 – 30% hydrochloropolysilanes. This stream may be further concentrated in a screw-conveyor, heated ball mill or paddle type drier to recover essentially all of the silicon tetrachloride and trichlorosilane, leaving a solid, flowable residue that may include small chunks, sometimes referred to herein as “powder  
20 residue,” containing the metal chlorides, unreacted silicon metal, traces of silica, non-volatile organics and the like as described in U.S. Patent 4,892,694 (Ritzer).

Various procedures have been disclosed to render the solid residue suitable for environmentally safe disposal. German Patent 21 61 641 discloses the reaction of a chlorosilane distillation residue with water vapor accompanied by the formation of  
25 hydrogen chloride. However, an adequate reaction takes place only with a stoichiometric excess of water vapor so that hydrochloric acid is produced from the excess water and hydrogen chloride which then also has to be treated before disposal. To avoid the formation of additional hydrochloric acid, U.S. Patent 5,066,472 proposed to perform the hydrolysis in the presence of additional hydrogen chloride and recycle the unreacted  
30 water.

U.S. Patent 4,690,810 discloses a process for the reaction of the chlorosilane residues with milk of lime to form a slurry of soluble calcium chloride and solid metal

- 4 -

hydroxides and oxides. That process does not allow for reclaiming any of the valuable chlorosilanes required to provide fluidity to the residue and further requires a procedure to convert the calcium chloride solution into a commercial form, else adding to the already great environmental load.

5           Other procedures have been proposed to treat residues from the purification of chlorosilanes such as are generated during the production of polycrystalline silicon. Those processes involve hydrolysis of the residues, and neutralization of the resulting hydrochloric acid followed by filtration to remove the co-product silica. That process involves the use of expensive acid resistant equipment and the high maintenance costs  
10 associated with the processing of corrosive hydrochloric acid. Filtration of the resulting slurries is difficult and many times is just not possible as the hydrolysis reactions form unfilterable gels and ultra-fine particles.

          The above-described processes, whether they concern the production of trichlorosilane, methylchlorosilanes, titanium tetrachloride or the rare earth chlorides,  
15 involve the step of contacting the residue with liquid water. The reaction of water with either the residual volatile metal chloride products or the metal chloride impurities contained within the residual solid metal or metal oxide results in the formation of corrosive hydrochloric acid. Therefore, the process equipment must be constructed of corrosion resistant materials. Leaks and spills provide a high likelihood of environmental  
20 contamination and worker exposure to corrosive materials. Furthermore, the aqueous hydrolysis of these metal chlorides results in the formation of solid metal oxides not only within the reaction mixture, but the solids can deposit on the interior portions of the equipment causing a process limiting build-up or plugging of pipelines, valves and other parts of the system.

25           Low cost procedures have now been found to maximize the recovery of valuable, moisture-reactive volatile compounds, while rendering the remaining residue non-hazardous for disposal or for recovery of valuable remaining metal impurities or catalysts. More particularly, methods for more economically processing the residues from chlorosilane production and/or other volatile metal chloride production processes to  
30 yield a waste product that can be readily disposed of, and preferably, to completely recover valuable volatile metal chlorides, have now been discovered. At least some of these methods allow an opportunity to reclaim valuable metals by well known extractive

- 5 -

metallurgy techniques. Also, the processes typically can be conducted without need for equipment constructed of the exotic metals or materials required to be resistant to the corrosion of hydrochloric acid.

By such procedures, residues can be dried and the volatile chlorosilanes and organochlorosilanes (hereinafter referred to collectively as "chlorosilanes"), titanium chlorides or other metal chloride products can be recovered for re-use while the non-volatile solids, containing water-reactive, low volatility metal chlorides, are treated with an alkali carbonate or bicarbonate humectant to produce a non-fuming, neutral solid. The neutral solid is suitable for environmentally safe disposal. Alternatively, the residue may be further processed by extractive metallurgy methods to recover valuable metals.

#### **Brief Description of Drawing**

The drawing figure is a schematic flow sheet of a process for the treatment of waste metal chlorides.

#### **Detailed Description**

Particular methods described herein proceed without the formation of a liquid waste product and may comprise:

- 1) Evaporating the volatile chlorosilanes or metal chlorides in a suitable continuous or batch type drier, optionally, in the presence of a chloride complexing agent,
- 2) Condensing the evaporated chlorosilanes or valuable, and volatile metal chlorides and making them available for complete recovery and re-use, thereby significantly increasing the overall yield, and
- 3) Subjecting the substantially non-volatile solid residues and residue metal chlorides to the action of selected alkaline hydrate solids at a temperature in excess of about 80°C (with most efficient operation at a temperature in the range of 120°C to 150°C) to yield a stable, neutral solid suitable for disposal or precious metal recovery.

The naturally occurring mineral, trona, is a usable alkaline hydrate material. Trona is inexpensive, readily available, and environmentally benign. The trona material used in the examples of this disclosure is T-200<sup>®</sup> mechanically refined trona sold by Solvay Mineral, Green River, WY. It is identified by CAS number

- 6 -

6106-20-3. Its chemical composition is nominally sodium carbonate (CAS 0497-19-8) 46%, sodium bicarbonate (CAS 0144-55-8) 36% and water (CAS 7732-18-5) 16%. T-200 trona is a powder having the following typical size characteristics:

5	<u>Sieve</u> <u>Opening</u>	<u>Typical</u> <u>Weight Percent</u>
	<70 $\mu\text{m}$	75
	<28 $\mu\text{m}$	50
	<6 $\mu\text{m}$	10

10

The drawing illustrates the production of a residue and its treatment with a trona material.

A stream (1) of solids-laden chlorosilane to be treated originates from the hydrogenation of silicon tetrachloride over a fluidized bed of metallurgical silicon, or from the hydrochlorination of silicon metal in a fluidized bed reactor using hydrogen chloride, or from the residues of the distillation processes that purify trichlorosilane and silicon tetrachloride produced from these reactions. One or more of these streams can be combined into an agitated slurry collection vessel (3) that serves as an intermediate storage vessel prior to feeding the slurry (5) to the treatment system. The composition of the slurry can vary considerably, but may consist of components as listed in Table I.

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- 7 -

Table I: Typical composition of waste chlorosilane/solid residue slurry

	Liquid Fraction, wt%	77.6
5	Trichlorosilane	2.2
	Silicon tetrachloride	83.6
	Cl <sub>6</sub> Si <sub>2</sub> O	14.2
	Solid Fraction, wt%	22.4
10	Silicon (elemental)	54.6
	Silica	19.1
	Chloride	16.1
	Iron	4.5
	Aluminum	2.9
15	Carbon	1.8
	Calcium	0.5
	Titanium	0.2
	Manganese	0.2
	Copper	0.1
20		

In the illustrated method, the crude slurry (5) is flowed into a batch drier vessel (7) equipped with paddle type mixer, bag filter (8), heating jacket, and solid discharge valve (12). Other mechanical methods of performing the evaporation of the volatile chlorosilanes are possible and this example is not meant to limit the scope of the invention.

The evaporation/concentration can be enhanced if a complexing agent is added to reduce the volatility of the aluminum chloride and ferric chloride components in the solid residue mixture. A readily available and well known complexing agent is finely ground sodium chloride as described in Fannin, A. A.; King, L. A.; Seegmiller, D. W.; Oye, H. A. *J. Chem. Eng. Data* 1982, 27(2), 114-119. The finely milled sodium chloride can be added to the charge of slurry. The amount of sodium chloride added is nominally at least twice the weight of the estimated amount of aluminum chloride and ferric chloride contained in the remainder of the slurry. The sodium chloride is useful in forming a chemical complex with the aluminum chloride and ferric chloride contained in the slurry. The salt complex lowers the vapor pressure of the aluminum chloride and thus helps to



- 8 -

retain the aluminum chloride and ferric chloride within the slurry solids while the volatile chlorosilane fraction is evaporated.

The charge of volatile chlorosilanes and mixed solids is sufficiently heated by a heating medium in the jacket of the drier to gasify the greater portion of the chlorosilanes; and the volatile chlorosilanes (14) are removed as a vapor. The chlorosilane vapors (16) are condensed in a condenser (9) and collected in a recovery vessel (10). A bag filter (8) may be employed on the drier to reduce the carry-over of fine particles with the chlorosilane vapors. In a preferred mode of operation, the drier may be recharged several times after the bulk of the chlorosilanes have been evaporated until the accumulated solids amount to about  $\frac{1}{4}$  of the working volume of the drier. At this point, the temperature of the drier is raised to complete the evaporation of the chlorosilanes, which, at atmospheric pressure, is a temperature of about 70°- 80°C.

The chlorosilanes collected in the receiver (10) may then be returned via a line (13) to the refining section of the chlorosilane production unit. The vent (14) from the drier is then switched to allow the vent gases (15) to pass to a suitable water spray scrubber (11) or similar treatment unit that is designed to remove residual amounts of hydrogen chloride from the vent gas stream.

A charge (2) of finely milled trona, natural sodium sesquicarbonate, is added to the drier (7) from a storage bin (4) via a lock chamber (6). The amount of trona to be added is such as to provide a pH greater than 7 in the residue solid. The optimum amount of trona to be added is generally determined by experiment since the composition of the residue material can vary. A modest excess of trona is desirable, but a greater excess presents only a minor additional cost. The mixture of dry solids and trona is heated to a temperature of between about 120° and 150°C, although higher temperatures may be used without negative effect. During the heating, hydrated moisture in the trona reacts with the metal chlorides and traces of chlorosilanes. Some HCl gas is formed, which reacts with the sodium carbonate portion of the trona. Additionally, as the trona is heated, it thermally decomposes to release additional moisture and carbon dioxide gas. The decomposition of the trona results in a porous solid which can readily react with the released hydrogen chloride gas. The released gas, mainly carbon dioxide, un-neutralized hydrogen chloride and excess moisture is vented to the scrubber (11).

- 9 -

The neutral, dry, free flowing solid consisting of the excess and decomposed trona, silicon metal, silica, and neutralized or hydrated metal chlorides is then cooled to a safe handling temperature and discharged via an outlet line (12). Provided sufficient trona has been used, the pH of a 10% aqueous slurry of the product solid is between 7 and 10.5 and no odor of hydrogen chloride is present in the dry solid.

The dry, neutral solids may be disposed of in a suitable landfill, or made available for recovery of selected metals using conventional extractive metallurgy methods.

Examples of suitable alkaline hydrates that may be used in the process are sodium or potassium sesquicarbonate, sodium aluminum sulfate dodecahydrate, sodium acetate trihydrate, sodium ammonium phosphate tetrahydrate, sodium carbonate decahydrate, sodium citrate dehydrate, sodium dihydrogen phosphate dehydrate, and mixtures of calcium carbonate or sodium carbonate, sodium bicarbonate, and/or other basic salts. In addition, inert hydrated minerals may be used such as Aluminite, Apophyllite, Bloedite, Chabazite, Gaylussite, Gmelinite, Heulandite, Kainite, Kieserite, Laumonite, Levyne, Mesolite, Mirabilite, Montmorillonite, Mordenite, Natrolite, Newberyite, Phillipsite, Scolecite, Stilbite, Struvite, and damp soil. In the case of damp soil, excess water content can cause processing difficulties; a water content of about 5% (w/w) is suitable for most purposes. Soil may be mixed with lime, trona or other alkaline solid to provide sufficient neutralizing strength. In order to satisfy the requirements for non-hazardous land fill disposal, the basic anion(s) is/are generally limited to sodium, potassium, calcium, and magnesium and excludes lithium, rubidium, barium, strontium, and the like.

Although not to be bound by theory of operation, it is believed that the successful working of the disclosed processes depends on water trapped in the solid hydrate. The trapped water is not released until it is exposed to the "waste" which contains, e.g., aluminum chloride and iron chloride, and traces of residual chlorosilanes. Upon exposure to metal chlorides in the waste, the hydrate is at least partially dehydrated by a transfer of water to the metal chlorides. The transferred water forms aluminum chloride hydrate (for example) and silica. The amount of the hydrate supplied and the water content thereof should be chosen to be sufficient to completely hydrate all the metal chloride in the waste.

- 10 -

As there is a small amount of HCl also liberated during this reaction and subsequently during long term exposure, it is best to react the HCl with an alkaline salt to at least partially neutralize the hydrogen chloride. The alkaline salt may be provided by using an alkaline hydrated mineral to react with the metal chlorides, or a separate alkaline salt may be provided. For example, in the alkaline hydrated mineral trona, sodium carbonate and bicarbonate are present in sufficient excess to serve as alkaline salts that react with the hydrogen chloride and form harmless salt, water and carbon dioxide. Calcium carbonate and magnesium hydroxide are examples of separate alkaline salts that could be added to neutralize HCl.

10 The resulting dry, neutral, and free flowing residue solid can be safely disposed of in an environmentally acceptable manner. After discharge of the neutralized solids, the drier is ready for a subsequent charge of chlorosilane slurry with out need for further clean-up.

The discharged solids, which meet the requirements for non-hazardous solid waste by the "TCLP" or Toxic Characteristic Leaching Protocol of 40 CFR §268.49 (2003), may be discarded in any suitable manner.

Alternatively, if valuable metals, such as copper, nickel, or silver, are used as catalysts or promoters in the production of chlorosilanes, or organochlorosilanes, the dry neutral solid residue can be made available for recovery of those metals by conventional hydrometallurgy extraction techniques. For example, if the alkali carbonate hydrate used in the process was trona, natural sodium sesquicarbonate, washing the neutralized solid residue with water would remove the bulk of the sodium carbonate and sodium chloride. Then the remaining solid could be acidified with sulfuric acid to form soluble copper sulfate. The copper sulfate could then be extracted by an organic solution of an oxime in kerosene as described in U.S. Patent 6,242,625.

Because moisture is carried into the process in the form of a hydrated solid, there is substantially no free moisture within the process. The water-reactive, low volatility metal chlorides, for example aluminum chloride, have a much stronger affinity for moisture than the alkali carbonate hydrate. Thus the environment within the drier is maintained in a state where no condensation of water or hydrochloric acid occurs, thus reducing the corrosive effect. Thus the drier can be constructed of a duplex stainless steel alloy such as Ferillium that is much less expensive than the

- 11 -

nickel/chromium/molybdenum alloys or glass enameled equipment that would otherwise be required.

#### Example 1

5           1,160 Kg of a slurry consisting of 25% solid silicon and metal chlorides and 75% of a mixture of silicon tetrachloride and trichlorosilane was added to a horizontal paddle type drier constructed of Ferillium duplex stainless steel and having a processing volume of 3.24 m<sup>3</sup>. The drier was further equipped with an integral bag filter on the process vapor outlet to retain fine particles and a condenser was provided downstream of the bag  
10 filter to condense and collect volatilized chlorosilanes. 36 Kg of Cargill Microsized 66 finely ground sodium chloride was also added. At essentially atmospheric pressure, heat was applied to the jacket of the drier and the bulk of the chlorosilanes were boiled off and condensed into a receiver. When the batch temperature began to rise above 60°C (the boiling point of silicon tetrachloride at process pressure), a fresh charge of 1,160 kg of  
15 slurry was made and the boiling continued. This fill, boil, fill sequence was repeated until a total of 4,211 kg of slurry had been charged. After the last slurry charge, the drier temperature was allowed to rise to 80°C to complete the evaporation of the chlorosilane. The drier vent was switched to a water spray vent scrubber and a charge of 250 kg of Solvay® T-200® finely ground trona, natural sodium sesquicarbonate, was added to the  
20 drier. The temperature of the drier was raised to 130°C over a period of one hour and held there for an additional two hours to assure complete reaction. The batch was cooled to less than 50°C and a fine gray powder solid was discharged to a bin. A 10% slurry of the powder in water indicated a pH of 10.3. The powder did not present any acidic odor, was free flowing and did not ignite when heated in air.

25

#### Example 2

A slurry consisting of 110 gram of solid residue from the hydrochlorination of silicon and 200 ml of silicon tetrachloride was placed in a 500 ml agitated flask that was fitted with several small TFE discs in the vapor path before a condenser. The slurry was  
30 gently heated to 80°C while the silicon tetrachloride was evaporated. 18 gram of sodium sesquicarbonate powder was added to the flask and the temperature was increased to 130°C. After holding the temperature for two hours, the flask was cooled and the

- 12 -

residual dry waste product had an indicated pH of 10.4. During the heating cycle, a yellow/white fume was collected on the TFE discs placed in the cooler portions of the apparatus. 160 mg of fume consisting of > 90% aluminum chloride with a minor amount of iron chloride were collected on the TFE discs.

5

### Example 3

A slurry consisting of 110 gram of solid residue from the hydrochlorination of silicon (containing 5.4% Al, 2.6% Fe), 15 gram of finely ground sodium chloride and 200 ml of silicon tetrachloride was placed in a 500 ml agitated flask fitted with several small discs of TFE mounted in the vapor path below the condenser. The flask was heated slowly to evaporate the silicon tetrachloride. When the temperature reached 63°C, no more vapors were being removed. Then 30 g of Solvay T-200 finely ground trona (natural sodium sesquicarbonate) were added and the heating continued up to 160°C. After cooling, the residual solids were free flowing and odor free. The pH was 9.9. During the heating cycle, there was a markedly lower amount of white fume noticed. The amount of fume collected on the TFE discs was reduced to 8.5 mg of aluminum chloride (from 160 mg in Example 2).

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### Example 4

From the production of methylchlorosilanes by the direct reaction of methylchloride and a copper catalyzed metallurgical grade silicon metal, a residue is produced. The residue consists of a solid fraction containing unreacted silicon metal with alloyed copper, metal chlorides such as aluminum chloride, ferric chloride, and other solid metal silicides and oxides. The liquid fraction contains a mixture of volatile and non-volatile methylchlorosilanes and methylpolysiloxanes. 100g of a slurry consisting of 5 g of solid fraction and 95 g of liquid methylchlorosilanes is charged to a flask having a paddle style agitator and a heating jacket. The flask is also fitted with a condenser and a receiver to collect the condensed vapors. The flask is heated to boil off the volatile methylchlorosilanes which are collected in the receiver. A second 100 g charge of slurry is made when the volume in the flask permitted, and is followed by a third 100 g charge in a similar manner. When the reaction flask reaches a temperature of 80°C, a flow of

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- 13 -

inert gas is begun to complete the evaporation of the volatile materials. A total of 250 gram of condensate is recovered.

The solid residue after having been held at 80°C under a inert gas purge is converted into a slightly coherent solid mass. The solid fumed in air and has the  
5 odor of hydrochloric acid.

To the solid residue is added 30 gram of finely ground sodium sesquicarbonate. There is a mild exotherm of about 5°C. The solid mixture is heated slowly to a temperature of 150°C over a period of a hour and then cooled to room temperature. The resulting mixture is a free flowing dark gray solid that had  
10 no detectable odor of hydrogen chloride. A water slurry of the solid indicates a pH of 7-10.

#### Example 5

From the manufacture of titanium tetrachloride by the chlorination of rutile  
15 ore, the "ash" from the chlorination process consists of unreacted oxides and non-volatile metal chlorides. 25 g of "ash" is added to an agitated reactor having a heating jacket and a solids addition funnel. The solids have a strong odor of chlorine and fumed mildly in moist air. Under an inert gas purge, the charge is heated to 80°C. At that point, 50 g of finely ground sodium sesquicarbonate is  
20 added to the mixer. The temperature of the mixer is slowly increased to 150°C under an inert gas purge. After cooling to room temperature, the solids remains free-flowing and has no significant odor. The pH of an aqueous slurry of the solids is between 7 and 10.

While the foregoing description and examples relate primarily to the treatment of  
25 residues of silicon hydrochlorination, chlorosilane distillation processes, titanium manufacture and methylchlorosilane processes, it should be appreciated that the methods described herein have broader applicability. The process could apply to other situations where a moisture-reactive volatile compound and a solid residue are to be separated, with the volatile compound to be recovered, and with the solid residue material to be rendered  
30 non-reactive to the normal ambient environment.

- 14 -

## Claims:

1. A method of processing a flowable solid material that includes at least one low volatility, water-reactive metal chloride, the method comprising:  
combining a flowable solid material that includes at least one low volatility,  
5 water-reactive metal chloride with a powdered hydrate to provide a mixture;  
heating the mixture at a temperature greater than 80° such that a low volatility, water-reactive metal chloride in the flowable solid material reacts with the hydrate; and  
discharging the resulting mixture for disposal or metals recovery.  
10
2. A method of claim 1 wherein the heating is carried out with the mixture further comprising milled sodium chloride.
3. The method of claim 1 wherein the power material contains at least one  
15 metal chloride selected from the group consisting of aluminum chloride, titanium chloride, vanadium chloride, chromium chloride, manganese chloride, iron chloride, cobalt chloride, nickel chloride, copper chloride, and zinc chloride.
4. The method of claim 1 wherein the flowable solid material is from the  
20 production of chlorosilanes.
5. The method of claim 1 wherein the flowable solid material is from the production of methylchlorosilanes.
- 25 6. The method of claim 1 wherein the flowable solid material is from the production of titanium chloride.
7. The method of claim 1 wherein the flowable solid material is from the production of hafnium and zirconium chloride.  
30
8. A method of processing the residue from a chlorosilane manufacturing process, the method comprising:

- 15 -

concentrating a residue mixture containing volatile chlorosilanes and lower volatility components including at least one water-reactive metal chloride in a drier unit suitable for processing a solid fraction;

separating volatile chlorosilane vapors from the mixture;

- 5       contacting the remaining substantially chlorosilane-free solid residue with a hydrate at a temperature greater than 80° such that the at least one water-reactive metal chloride reacts with the hydrate; and
- discharging the resulting powder mixture.

- 10       9. The method of claim 8 further comprising contacting the substantially chlorosilane-free solid residue with an alkaline salt to increase the pH of the resulting powder mixture.

10. The method of claim 8 further comprising, simultaneously:

- 15       contacting the remaining substantially chlorosilane-free solid residue with a hydrate; and
- contacting the remaining substantially chlorosilane-free solid residue with the alkaline salt.

- 20       11. The method of claim 10 wherein the contacting of the remaining substantially chlorosilane-free solid residue with a hydrate and the contacting of the remaining substantially chlorosilane-free solid residue with the alkaline salt is accomplished by contacting of the remaining substantially chlorosilane-free solid residue with mechanically refined trona, which is a natural form of sodium
- 25       sesquicarbonate, is a hydrated mineral, and provides an alkaline salt.

12. The method of claim 8 wherein:

the alkaline salt comprises calcium carbonate; and

the hydrate comprises damp natural soil.

30

13. The method of claim 8 wherein:

the alkaline salt comprises magnesium hydroxide; and



- 16 -

the hydrate comprises montmorillonite clay.

14. The method of claim 8 wherein the residue mixture contains at least one metal chloride selected from the group consisting of aluminum chloride, titanium  
5 chloride, vanadium chloride, chromium chloride, manganese chloride, iron chloride, cobalt chloride, nickel chloride, copper chloride, and zinc chloride.

15. A method of processing the residue from a chlorosilane manufacturing process, the method comprising:

10 concentrating a residue mixture containing volatile chlorosilanes and lower volatility components including at least one water-reactive metal chloride in a drier unit that is suitable for processing a solid fraction in the presence of finely milled sodium chloride;

separating volatile chlorosilane vapors from the mixture in the drier unit;

15 contacting the remaining substantially chlorosilane-free solid residue with a hydrate in the drier unit at a temperature greater than 80° such that the at least one water-reactive metal chloride reacts with the hydrate; and

discharging the resulting powder mixture from the drier unit.

20 16. The method of claim 15 further comprising contacting the substantially chlorosilane-free solid residue with an alkaline salt to increase the pH of the resulting powder mixture.

25 17. The method of claim 16 further comprising simultaneously contacting the remaining substantially chlorosilane-free solid residue with a hydrate and contacting the remaining substantially chlorosilane-free solid residue with the alkaline salt.

30 18. The method of claim 17 wherein the contacting of the remaining substantially chlorosilane-free solid residue with a hydrate and the contacting of the remaining substantially chlorosilane-free solid residue with the alkaline salt is accomplished by contacting of the remaining substantially chlorosilane-free solid

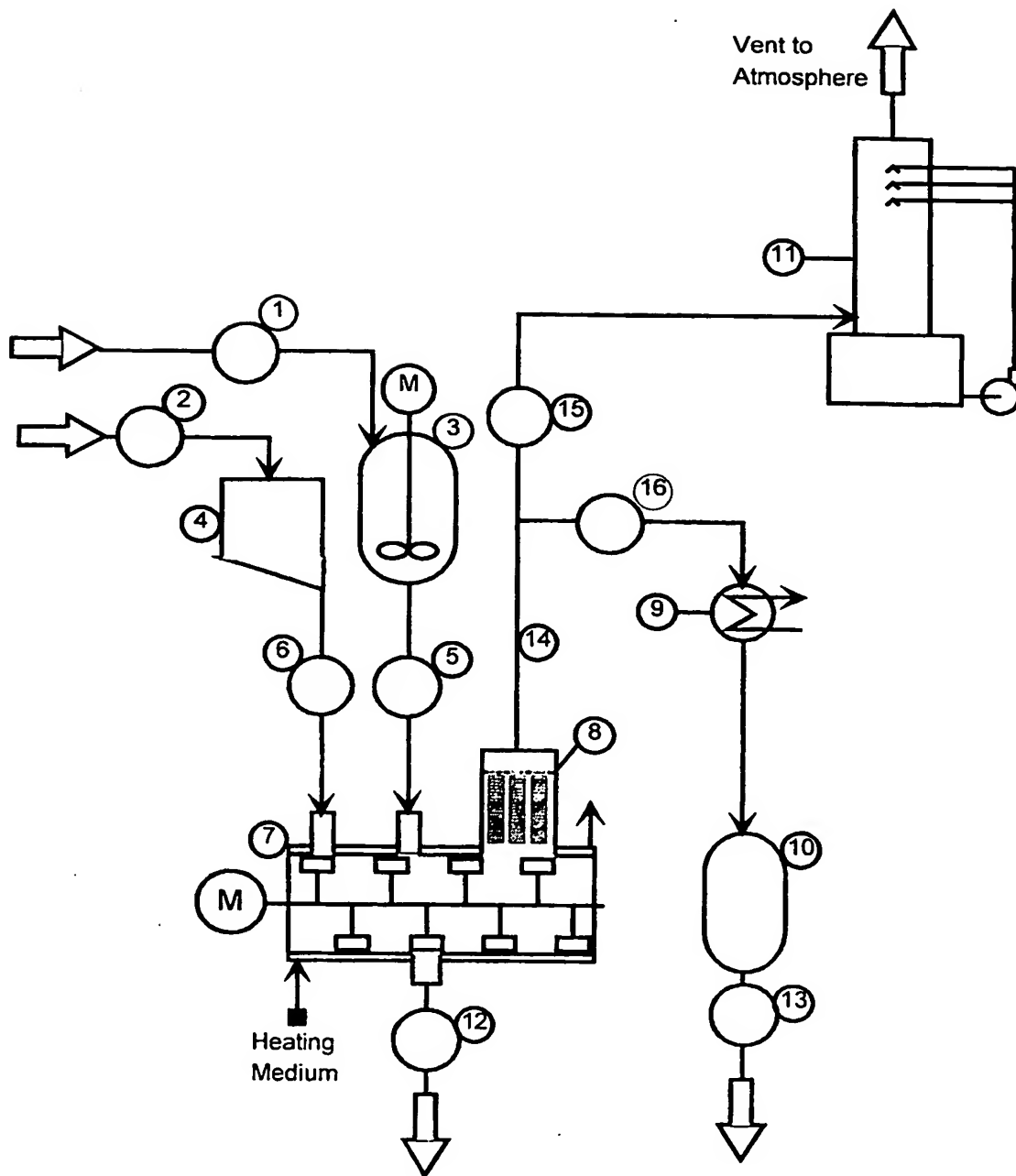
- 17 -

residue with trona, which is a natural form of sodium sesquicarbonate, is a hydrated mineral, and provides an alkaline salt.

5           19. The method of claim 15 wherein:  
the alkaline salt comprises calcium carbonate; and  
the hydrate comprises damp natural soil.

10           20. The method of claim 15 wherein:  
the alkaline salt comprises magnesium hydroxide; and  
the hydrate comprises montmorillonite clay.

15           21. The method of claim 15 wherein the at least one metal chloride is at least  
one metal chloride selected from the group consisting of aluminum chloride,  
titanium chloride, vanadium chloride, chromium chloride, manganese chloride, iron  
chloride, cobalt chloride, nickel chloride, copper chloride, and zinc chloride.



• Figure 1

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/21267

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01B 33/107, 33/113  
US CL : 423/341,342,343,335,481

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/341,342,343,335,481

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EAST search: chloride, trona, carbonate, water, react

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,878,291 A (KELLER et al) 15 April 1975 (15.04.1975), abstract, Figure.	1-21
A	US 4,200,618 A (PITTS) 29 April 1980 (29.04.1980), abstract.	1-21
A	US 4,690,910 A (BRENEMAN et al) 01 September 1987 (01.09.1987), claim 1.	1-21
A	US 4,676,967 A (BRENEMAN) 30 June 1987 (30.06.1987), claim 1, Figure.	1-21
A	US 5,931,773 A (PISANI) 03 August 1999 (03.09.1999), abstract, claim 1.	1-21

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

15 December 2003 (15.12.2003)

Date of mailing of the international search report

31 MAR 2004

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

N. M. Nguyen

Telephone No. 571-272-1700

# PATENT COOPERATION TREATY

Advanced Silicon/RJP

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

## NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

To:  
RICHARD J. POLLEY  
KLARQUIST SPARKMAN, LLP  
ONE WORLD TRADE CENTER, SUITE 1600  
121 SW SALMON STREET  
PORTLAND, OR 97204

Date of Mailing  
(day/month/year)

31 MAR 2004

Applicant's or agent's file reference  
3468-65972

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.  
PCT/US03/21267

International filing date  
(day/month/year)  
07 July 2003 (07.07.2003)

Applicant  
ADVANCED SILICON MATERIALS LLC

1. ☒ The applicant is hereby notified that the international search report has been established and is transmitted herewith.

### Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

Where? Directly to the International Bureau of WIPO, 34, chemin des Colombettes  
1211 Geneva 20, Switzerland, Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

DOCKETED FOR:

6-30-04

COMPUTER ☒

CARD ☒

BOOK ☒

DRAWER ☒

BKPR ☒

ANN. SVE ☒

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

- ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.  
☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

### 4. Reminders

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90 bis.1 and 90 bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later); otherwise the applicant must, within 20 months from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of 30 months (or later) will apply even if no demand is filed within 19 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the ISA/US  
Mail Stop PCT, Attn: ISA/US  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450  
Facsimile No. (703) 305-3230

Authorized officer

N. M. Nguyen

Jean Inocencio  
Paraguay: Special

Telephone No. 571-272-1700

Form PCT/ISA/220 (April 2002)

(See notes on accompanying sheet)

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 3468-65972	<b>FOR FURTHER ACTION</b>	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/US03/21267	International filing date ( <i>day/month/year</i> ) 07 July 2003 (07.07.2003)	(Earliest) Priority Date ( <i>day/month/year</i> ) 01 April 2003 (01.04.2003)
Applicant ADVANCED SILICON MATERIALS LLC		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the Report**

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (See Box II).

4. With regard to the title,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the abstract,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No. \_\_\_\_\_



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/21267

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01B 33/107, 33/113

US CL : 423/341,342,343,335,481

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U.S. : 423/341,342,343,335,481

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EAST search: chloride, trona, carbonate, water, react

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 4,676,967 A (BRENNEMAN) 30 June 1987 (30.06.1987), claim 1, Figure.	1-21
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☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\* & \* document member of the same patent family

Date of the actual completion of the international search

15 December 2003 (15.12.2003)

Date of mailing of the international search report

31 MAR 2004

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US

Commissioner for Patents

P.O. Box 1450

Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

N. M. Nguyen

Telephone No. 571-272-1700

**Box No. VIII (iv) DECLARATION: INVENTORSHIP (only for the purposes of the designation of the United States of America)**

*The declaration must conform to the following standardized wording provided for in Section 214; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box VIII (iv). If this Box is not used, this sheet should not be included in the request.*

**Declaration of inventorship (Rules 4.17(iv) and 51bis.1(a)(iv))  
for the purposes of the designation of the United States of America**

I hereby declare that I believe I am the original, first and sole (if only one inventor is listed below) or joint (if more than one inventor is listed below) inventor of the subject matter which is claimed and for which a patent is sought.

This declaration is directed to the international application of which it forms a part (if filing declaration with application).

This declaration is directed to International Application No. \_\_\_\_\_ (if furnishing declaration pursuant to Rule 26ter).

I hereby declare that my residence, mailing address, and citizenship are as stated next to my name.

I hereby state that I have reviewed and understand the contents of the above-identified international application, including the claims of said application. I have identified in the request of said application, in compliance with PCT Rule 4.10, any claim to foreign priority, and I have identified below, under the heading "Prior Applications," by application number, country or Member of the World Trade Organization, day, month and year of filing, any application for a patent or inventor's certificate filed in a country other than the United States of America, including any PCT international applications designating at least one country other than the United States of America, having a filing date before that of the application on which foreign priority is claimed.

**Prior Applications:**

I hereby acknowledge the duty to disclose information that is known by me to be material to patentability as defined by 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the PCT international filing date of the continuation-in-part application.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**Name:** BRENEMAN, William C.

**Residence:** Moses Lake, Washington  
(city and either US state, if applicable, or country)

**Mailing Address:** 1103 S. Skyline Drive, Moses Lake, Washington 98837, United States of America

**Citizenship:** US

**Inventor's Signature:** William C. Breneman  
(if not contained in the request, or if declaration is corrected or added under Rule 26ter after the filing of the international application. The signature must be that of the inventor, not that of the agent)

**Date:** 14 July 2003  
(of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26ter after the filing of the international application)

**Name:**

**Residence:**  
(city and either US state, if applicable, or country)

**Mailing Address:**

**Citizenship:**

**Inventor's Signature:** .....  
(if not contained in the request, or if declaration is corrected or added under Rule 26ter after the filing of the international application. The signature must be that of the inventor, not that of the agent)

**Date:** .....  
(of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26ter after the filing of the international application)

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (iv)".